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Exchange of nutrients across the sediment-water interface in intertidal ria systems (SW Europe)

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ABSTRACT

Concentrations of nitrate, nitrite, ammonium, phosphate and silicate were determined in river water, tidal water that floods the intertidal sediment (flooding water) and pore water of those sediments in the Northern Galician Rias of Ortigueira and Viveiro (NW Iberian Peninsula). The field surveys were done in the productive seasons of spring and summer 2008. Short-sediment cores and tidal flooding water were sampled at the intertidal area during the first 20 minutes that the tide inundates the sampling site. Nutrient fluxes of rivers (Lourido and Landro) flowing into the rias were in the order of $H_4SiO_4 > NO_3^- > NH_4^+ > HPO_4^{-2}$. Nutrients inputs from those rivers were low relative to the nutrient discharge of the entire coastal area. Striking changes of nutrient concentrations in flooding and pore waters of intertidal sediments were observed in the short periods of tidal inundation. Nutrient fluxes driven by molecular diffusion and tide-induced transport across the sediment-water interface were quantified and compared to the nutrient river contribution. Diffusive fluxes ranged from 9.3 to 13.7 $nmol \cdot cm^{-2} \cdot d^{-1}$ for nitrate and nitrite, -1.32 to 30.1 $nmol \cdot cm^{-2} \cdot d^{-1}$ for ammonium, -0.01 to 0.49 $nmol \cdot cm^{-2} \cdot d^{-1}$ for phosphate, and -13.2 to 0.2 $nmol \cdot cm^{-2} \cdot d^{-1}$ for silicate. Tide-induced transport always exceeded diffusive fluxes, with differences reaching up to four orders of magnitude for silicate. The overall results of this study emphasize the relevance of tidal water movement in promoting the sediment-water exchange of nutrients in intertidal sub-ecosystems.

Keywords: Flooding water; pore water; benthic fluxes; diffusive fluxes; pore water advection, Northern Galician Rias

1. Introduction

Physical and biogeochemical processes occur at various temporal and spatial scales in coastal areas (Geyer et al., 2000). Biogeochemical cycling of nutrients in coastal zones under land-ocean interactions is strongly conditioned by fluxes into, through, and out of rivers. The river system store and transform the elements in transit, such that fluxes and chemical forms of materials finally exported are often quite different from those encountered in the headwaters (Richey, 1983).

In meso and macro-tidal ecosystems, the semi-diurnal tidal regime implies that the intertidal zone is twice a day covered and uncovered (Vranken and Oenema, 1990; Portnoy and Giblin, 1997), generating non-steady state conditions between solids and pore water (Rocha, 1997; Hammond et al., 2001). When sediments are covered with tidal water, solute transport across the sediment-water interface is driven by various mechanisms, such as diffusion, pore water advection, bioirrigation and bioturbation.

Nutrients fluxes due to diffusion have been quantified in estuarine and coastal areas in several studies (e.g. Callender and Hammond, 1982; Gomez-Parra and Forja, 1993; Watson et al., 1993; Zabel et al., 1998; Serpa et al., 2007). However, nutrient transport associated to dynamic events (i.e. advective transport, resuspension, etc), has been studied to a lesser extent (Billerbeck et al, 2006; Huettel et al., 1998; Jahnke, 2003; Deborde et al., 2008; Ibánhez et al., 2011).

In contrast to subtidal sediments, the intertidal sediment is submitted to different conditions of light, temperature and pressure. On the other hand, during both flood and ebb tides, the flowing water interacts with the sediment pore water (Caetano et al., 1997; 2007; Rocha, 1997; Huettel et al., 1998). The way in which water floods the intertidal area is rather complex, during the first minutes of the inundation process sediment may be resuspended and seawater mixed with pore water of surface sediment layers. The result is a change in the composition of the surface water, previously achieved during the air-exposed situation (Falcão and Vale, 1998; Huettel et al., 1998; Jahnke, 2003). This change may increase the nutrient exchange, which coupled with benthic regeneration, can support the nutrient

demand of primary producers (Nixon et al., 1976; Fisher et al., 1982; Boynton and Kemp, 1985)

This work aimed to quantify the contribution of intertidal sediments to the nutrient budget of two Northern Galician Rias (Iberian Peninsula, SW Europe). These rias are coastal inlets with an external open area dominated by marine processes and a partially enclosed estuarine shallow area (Evans and Prego, 2003). The estuarine area, referred to the inner ria, is characterized by large intertidal sedimentary areas. While in winter the strong freshwater inputs dominate the hydrography of these systems (Augas de Galicia, 2011), the oceanographic upwelling-downwelling events dominate in summer (Alvarez et al., 2010; Ospina-Alvarez et al., 2010). Most studies have considered that nutrient regeneration in this area is driven by these processes (Alvarez-Salgado et al., 1996; Prego et al., 1999; Prego, 2002; Varela et al., 2005).

The extended intertidal sedimentary areas of these rias make them ideal field laboratory to better assess the importance of sediment contribution to the nutrient budget. Sampling was done during the productive seasons, spring and summer of 2008. The study reports concentrations of ammonium, nitrate, nitrite, phosphate and silicate in river water, sediment pore water and overlying water at low tide and in a short period of the tidal inundation over sediments from Ortigueira and Viveiro rias. The nutrient contribution to the ria was estimated. Additionally, diffusive and advective transport of nutrients across the sediment-water interface of intertidal sediments was calculated. To our knowledge the magnitude of the three contributions to the total nutrient budget in the water column is discussed for the first time in ria-coastal systems.

2. Materials and methods

2.1 Study area

At the northerly point of the Iberian Peninsula are located the rias of Ortigueira and Viveiro (Figure 1), which are part of the Northern Galician Rias (Torre-Enciso, 1958). The Ria of Ortigueira and Ria of Viveiro are mesotidal systems with a surface area of respectively 38 and 27 km^2, from which 48% and 11% correspond to intertidal areas.

The Mera River (annual average flow: 6.0$m^3 \cdot s^{-1}$) and Lourido Stream (0.5 $m^3 \cdot s^{-1}$) discharge into the Ria of Ortigueira and the Landro River (7.1 $m^3 \cdot s^{-1}$) into the Ria of Viveiro. The flows of these rivers exhibit a pronounced seasonal signal with the highest discharges in winter and spring and the lowest in summer. Figure 2 presents the variation of the Lourido and Landro discharges registered in 2008. Bottom sediments of rias consist of a mixture of fine sands and mud. The area has low population density (≈70 inhabitants$\cdot km^{-2}$) and no massive industrial activity.

2.2 Sampling of sediment and overlying water in rias

Water and sediment were sampled on spring (9th and 10th April) and summer (21st and 22nd July 2008) in intertidal areas of the Ortigueira and Viveiro rias. The two sampling periods corresponded to contrasting river discharges (Figure 2): 2.6 and 0.1 $m^3 \cdot s^{-1}$ for Lourido Stream, and 85 and 5 $m^3 \cdot s^{-1}$ for Landro River. At low tide when sediment was exposed to the atmosphere water was collected from the main channel of both rias using acid pre-cleaned syringes with 0.45 μm polycarbonate filter. Around 1 m apart from the water-sampling site, sediments were sampled at the Ria of Ortigueira (La Caleira-Inlet, 43°42.82'N-7°52.69'W; Figure 1) with a methacrylate core (30 cm length, 6 cm diameter) and then quickly sliced in 2 cm layers. Sediment core sections (n=4) were stored in acid pre-cleaned HDPE vials avoiding air presence inside and kept in refrigerated atmosphere until processing at the onshore clean portable-laboratory. At the Ria of Viveiro (Landro Mouth, 43°40.09'N-7°35.66'W; Figure 1) topmost (≈3 cm) sandy sediments were collected with pre-cleaned plastic spatula and packed into plastic bags.

When tidal water starts to flood each site, a sample of intertidal sediments and water were collected at each time of inundation: 5, 10, 15, and 20 min. Tidal inundation water, hereafter referred as flooding water, was sampled 1 cm above the sediment surface directly into acid pre-cleaned syringes and filtered with 0.45 μm polycarbonate membranes. Sediments were collected in the same way as during air exposure of the intertidal area. Five sediment cores were sampled at the Ria of Ortigueira, at air-exposed conditions (n=1) and subsequent times (n=4).

Immediately after sampling, the sediment layers were stored into pre-cleaned 50 mL Eppendorf® tubes avoiding the presence of air inside. Sampling was done by a

team of four people, taking place in less than 3 minutes per core collection. Sediments were centrifuged at the laboratory with a UniCen 15D (Herolab) at 4500 rpm for 5 to 20 minutes at 4°C. No significant changes on redox sensitive elements were found with this sampling procedure (Caetano et al., 1995). After centrifugation, the supernatant, hereafter referred as pore waters, were removed from sediments with plastic syringes, filtered through a polycarbonate filter (0.45 μm) in a laminar flow cabinet (ISO Class 5) and stored in 50 mL polyethylene bottles. All the waters samples were preserved under refrigeration until analysis.

2.3 Sampling of river waters

Lourido Stream and Landro River were sampled three times, prior to each sampling of sediments and flooding water. The rivers were sampled at the same site on January 21st, February 20th, March 17th, May 19th, June 17th and July 15th, 2008. Water was collected into 50 mL polyethylene bottles previously cleaned and washed with HCl acid, and immediately frozen at -20°C to determine nitrate, nitrite, ammonium and phosphate. In order to avoid the formation of polymers in cold fresh water samples (Kobayashi, 1966), silicate samples were taken in 10 mL plastic bottles and preserved at 4°C until analysis.

2.4 Analytical methods

Water temperature and salinity were measured *in situ* using a WTW MultiLine P4 Set (error range ±0.1), calibrated with standard solutions before sampling. Nutrient measurements in river water, flooding water and pore water were carried out in triplicates using an Integral Futura autoanalyzer system (Alliance Instruments) with separate lines for nitrate, nitrite, ammonium, phosphate and silicate in agreement with the standard colorimetric methods (Hansen and Koroleff, 1999). Detection limits as three times the standard deviation of 10 replicate measurements of reagent blank, were: 0.14 μM for NO_3^-, 0.002 μM for NO_2^-, 0.01 μM for NH_4^+, 0.08 μM for HPO_4^{-2} and 0.14 μM for H_4SiO_4.

The first two centimeters of the collected sediment cores were dried at 50°C during one week until constant weight and porosity was calculated according to Berner (1980) with the equation:

$$\phi = \frac{W_{pw}}{W_{pw} + \left(\frac{W_s}{G_s}\right)} \quad (1)$$

where Φ is the porosity, W_{pw} is the weight of the pore water expressed in grams, W_s is the weight in grams of the dry sediment and G_s is the specific gravity of the sediment, which is assumed as a constant of 2.65 (Vanoni, 2006). The obtained sediment porosity for the rias of Ortigueira and Viveiro was 0.73 and 0.44, respectively. Additional grain-size analyses were performed in superficial sediments from both rias by dry sieving (Retsch AS-200). Sediments were grouped into mud, sand and gravel fractions, following the Udden-Wentworth scale.

2.5 Estimation of sediment-water exchange

Diffusive fluxes (DF) across the sediment-water interface were estimated according to Fick's first law of diffusion (Berner, 1980) using the equation:

$$DF = - \phi^3 \cdot D_0 \cdot \left[\frac{C_{pw} - C_{fw}}{\Delta x}\right] \quad (2)$$

where Φ is the porosity (dimensionless); D_0 is the diffusion coefficient of a solute at a given temperature ($cm^2 \cdot s^{-1}$); C_{pw} is the nutrient concentration (μM) in pore water of the topmost sediment layer at t=20; C_{fw} is the nutrient concentration (μM) in flooding water; and Δx is the thickness of the water-sediment diffusion layer (equal to 1.5 cm in this study which is equivalent to the distance across the interface where concentrations were measured). Diffusion coefficients (D_0) for NO_3^-, NO_2^-, NH_4^+ and HPO_4^{2-} and H_4SiO_4 were calculated on the basis of data obtained by Li and Gregory (1974), Lerman (1979) and Callender and Hammond (1982) at 0, 18 and 25°C, by linear interpolation based on known coefficients at a given temperature with the temperature measured in the sampling days.

D_0 values used *to* calculate diffusive fluxes were*:* on April (temperature 9.6 ± 0.1 °C), NO_3^- = 13.23 x 10^{-6}, NO_2^- = 10.74 x 10^{-6}, NH_4^+ = 13.58 x 10^{-6}, HPO_4^{2-} = 2.82 x 10^{-6}, and H_4SiO_4 = 3.88 x 10^{-6} $cm^2 \cdot s^{-1}$; and July (temperature 19.0 ± 0.1 °C): NO_3^-

= 16.68 x 10^{-6}, NO_2^- = 15.87 x 10^{-6}, NH_4^+ = 17.34 x 10^{-6}, HPO_4^{2-} = 5.59 x 10^{-6}, and H_4SiO_4 = 7.70 x 10^{-6} $cm^2 \cdot s^{-1}$.

Fluxes obtained in Eq. 2 ($nmol \cdot cm^{-2} \cdot s^{-1}$), were converted to daily fluxes per square centimeter ($nmol \cdot cm^{-2} \cdot d^{-1}$), considering that each day has two tidal cycles. Thus the sediment is covered during two periods of the day.

Tide-induced transport (T_t) was estimated based on the following equation (Eq. 3) that estimate the solute variation during the tidal inundation period (Caetano et al., 2007):

$$T_t = \sum \left[\left(\frac{C_{t2} - C_{t1}}{2} \right) - C_r \right] \cdot \left(h_{t2} - h_{t1} \right) \qquad (3)$$

where C_{t2} and C_{t1} are the nutrient concentration in the pore water (μM) at each sampling time (t_1, t_2, t_3, t_n), C_r is the residual concentration in μM (lowest value measured in coastal waters for the sampling area), and h is the water depth (cm) at the same times. Tide-induced transport of nutrients was calculated for the first 20 minutes of inundation. Since intertidal sediments are inundated twice a day (semi-diurnal tidal regime) the processes induced by tidal flooding of intertidal sediments also occurred in two daily episodes. Thus the estimated tidal induce transport was converted per unit of area and as daily fluxes ($nmol \cdot cm^{-2} \cdot d^{-1}$). Positive values indicate an export from the sediment to the overlying water. Water depth and tide height at the sampling area were determined by barometric difference using data measured with an AQUAlogger 520 sensor (Aquatec).

A rough estimation of the flux of nutrients from the rivers to the rias ($nmol \cdot cm^{-2} \cdot d^{-1}$, Table 2) was estimated by multiplying the nutrient fluxes (Q·C) by the surface of the rias (S) according to the equation:

$$RF = \left[\frac{Q \cdot C}{S} \right] \qquad (4)$$

where Q corresponds to the river flow ($m^3 \cdot s^{-1}$) and C is the nutrient concentrations (μM) in the river waters.

Using (*i*) satellite images, (*ii*) water velocity of the river in the central channel of the ria ($m \cdot s^{-1}$), and (*iii*) 3D profiles of each ria, the surface of the Ortigueira and

Viveiro rias was calculated considering the influence of the Lourido and Landro River, respectively (Fig. 1a and 1b). First it was calculated the horizontal distance that the river plume reaches during a tidal cycle, from the intertidal area to the central channel of the ria (by means of *i* and *ii*), and then its equivalent area in km^2 was calculated (by means of *iii*). The surface (S in Eq. 4) was equivalent to 0.686 km^2 for the Ria of Ortigueira and 0.378 km^2 for the Ria of Viveiro. Fluxes obtained in Eq.4 were adjusted to a daily scale and finally expressed as $nmol \cdot cm^{-2} \cdot d^{-1}$.

Surface water velocity ($m \cdot s^{-1}$) was monitored with a Valeport 808 electromagnetic current meter throughout 2008 (n=48). Daily river flows (Q) were provided by Augas de Galicia (Consellería de Medio Ambiente-Xunta de Galicia), and corrected for the total river basin (Figure 2). 3D profiles of the rias were done with Surfer software by means of grid volume computations (Golden Software, 2009).

2.6 Statistics

Differences in nutrient concentration between river samples were checked using a two-tailed t-test and nutrient variability during sampling periods by means of an F-test. A non-parametric Wilcoxon-Mann-Whitney analysis (Ott and Longnecker, 2008) was used to evaluate differences between nutrient concentration and fluxes in flooding and pore waters during the sampling dates. All the statistical analyses were carried out using GraphPad Prism 4.0 for Mac OS-X (GraphPad Software Inc, 2004).

3. Results

3.1 Nutrient contribution from rivers

Table 1 gives the ranges of nitrate, nitrite, ammonium, phosphate and silicate concentrations in waters of Lourido Stream and Landro River. Significant differences in concentration of nitrate (t-test: $t = 2.76$, $df = 9$, $p < 0.05$) and silicate (t-test: $t = 3.96$, $df = 4$, $p < 0.05$) were observed between the Lourido Stream and Landro River. Nitrite and nitrate concentrations for each river were relatively constant during the two studied periods. One of the most remarkable aspects was that Lourido Stream showed no significant differences in silicate concentrations between periods, while enhanced silicate values were observed in the period of May-July for the Landro River (up to 246 μM) as shown in Table 1.

3.2 Nutrient contribution from sediments

3.2.1 Muddy sediments (Ria of Ortigueira)

Sediments from the inner part of the ria were characterized by high mud content (≈99% grain size <63*μ*m). The depth profiles of nutrients in pore waters of air-exposed sediments in the two sampling dates showed similar trends. Concentrations increased with the depth and, in general, reached higher values at 6-8 cm depth than in the surface layers (Figure 3). Nutrient concentrations in flooding water and sediment pore water were, in general, higher in spring than summer, with exception of phosphate (Figure 4a). The lowest concentrations of phosphates were found in April (water temperature: 9.6°C) and the highest in July (water temperature: 19.0°C).

Differences in nutrient concentrations in pore water between April and July were significant at $p < 0.05$ (Mann-Whitney test) for ammonium and phosphate.

The pattern of concentration in flooding water and pore water was different for each nutrient as shown in Figure 4a. Nitrate and nitrite displayed higher values in the flooding water (April: 26-74 μM, July: 0.8-10 μM) than in the pore water (April: 1.7-9.2 μM, July: 1.4-2.0 μM). This difference was up to thirty times higher in April than in July. An opposite behavior was observed for ammonium (flooding water, April: 3-18 μM, July: 1-2 μM; pore water, April: 55 to 113 μM, July: 20 to 50 μM) and phosphate (flooding water, April: 0.2-0.8 μM, July: 0.3-0.6 μM; pore water, April: 0.2-1.4 μM, July: 3.0-6.2 μM) with the highest concentrations in the pore water for both sampling dates. Silicate in flooding (74-128 μM) and pore waters (49-71 μM) followed a similar pattern to nitrate and nitrite in spring, with higher values in the flooding water. Conversely, this pattern changed in summer (flooding water: 15-61 μM; pore water: 59-78 μM) since silicate concentrations in the flooding water decreases.

During spring, nitrate and nitrite in flooding water increased sharply in the first 5 minutes of inundation remaining high for 5 more minutes (74 μM). Conversely, concentrations in pore water decreased three fold during the first 5 minutes of inundation. In contrast, concentrations of ammonium in flooding waters decreased in the first 5 minutes of inundation while those of pore water increased in the same period from 55 to 112 uM. Afterwards concentrations decreased gradually close to the initial values. Phosphate in flooding and pore water decreased within the first 5

minutes of inundation and remained relatively constant (≈3 μM) for the remaining 20 min of flooding. Maximum silicate concentration in flooding water was found at t=5 (128 μM), preceded by a sharp rise. A decline of 42% in silicate concentrations was observed between 5 and 15 minutes after inundation followed by a new increase in silicate concentrations (up to 115 μM). In pore water silicate had a similar trend, although with attenuated variations and a peak concentration of 71 μM at 10 minutes of inundation.

During summer, concentrations of nitrate and nitrite in the flooding water were 12 times lower after inundation as compared with values founded before tidal incursion. Pore water concentrations were constant around 1.8 μM. As observed in April, concentrations of ammonium were higher in pore waters than in flooding waters. Ammonium concentrations in flooding water were low (≈2 μM) and slightly variable. Unlike in April, concentrations in pore waters decreased at the beginning of inundation from 39 to 20 μM increasing again to 38 μM at 15 minutes. Concentrations of phosphate in pore water increased during the first 15 minutes (up to 6.2 μM) decreasing afterwards to values similar with those observed before the tidal inundation. Concentrations in flooding water were low and relatively constant (0.3-0.6 μM) with time. Silicate in flooding and pore water had similar concentrations before the arrival of the tide (≈66 μM). However, concentrations in pore water remained relatively constant, while in flooding water decreased gradually to 23 μM.

3.2.2 Sandy sediments (Ria of Viveiro)

The sediment cover of the studied area at the inner part of the ria is predominantly sandy (96% of grain size >63μm). Vertical core samples were not taken in the Ria of Viveiro because of difficulty in collecting cores in sandy sediments at this station. Consequently, temporal differences of nutrient concentrations in pore water represent just the first 3-cm sediment layer.

Nutrient concentrations in flooding and pore water at the Ria of Viveiro were mostly elevated in spring than summer, although silicate showed an inverse behavior (Figure 4b). Nitrate and nitrite, phosphate and silicate in pore water were significantly different between April and July (Wilcoxon-Mann Whitney test, $p < 0.05$).

Nitrate and nitrite displayed minor differences between mean concentrations in flooding and pore water (April, flooding water: 15-40 μM, pore water: 34-58 μM; July,

flooding water: 14-24 µM, pore water: 6-18 µM). Ammonium in flooding and pore water behaved quite differently in spring and summer: concentrations in flooding water ranged between 17 and 26 µM in April and between 4 and 9 µM in July; and in pore water between 9 and 24 µM in April and 4 and 13 µM in July. Phosphate in pore water was higher than flooding water in both dates (April, flooding water: 0.2-0.5 µM, pore water: 2.8-8.2 µM; July, flooding water: 0.3-0.8 µM, pore water: 1.1-2.0 µM). However, this difference was only four times in the summer in contrast with the high differences observed in spring (>15 times). Time variation patterns of silicate concentrations in flooding water were different between sampling dates. During spring, values were slightly higher in pore water (flooding water: 0.4-2.4 µM, pore water: 2.4-3.4 µM), but in summer, it was presented an inverse behavior (flooding water: 38-68 µM, pore water: 6-11 µM), with values six times higher in flooding water.

In spring, opposite temporal variation patterns were found for nitrate and nitrite concentrations in flooding water and pore water. Concentration increase in flooding waters corresponds to the decrease in pore waters. After 5 minutes of inundation values reached 36 µM, remaining relatively constant (34 to 43 μM) during the studied period. Ammonium in flooding water increased 53% during the first 5 minutes of inundation decreasing gradually thereafter, re-establishing concentrations measured at t=0. The time course evolution of ammonium in pore water was irregular. Values decreased between 5 and 15 minutes of inundation (up to 9 µM) followed by an increase at the end of inundation. Phosphate concentrations in flooding water were relatively constant (0.2 to 0.5 µM), whereas in pore water values decreased gradually from 8.2 µM to 2.8 µM. Silicate values in both flooding water and pore water showed a minor variation being in average 1.3 and 2.6 μM, respectively.

In summer, nitrate and nitrite in flooding water was around 1.3 µM, while in pore water irregular changes were observed, with the minimum concentration at 10 minutes of inundation (2.4 µM). Ammonium concentrations in flooding water decline 49% during the first 5 minutes of inundation remaining close to 4.4 µM. In pore water, maximum ammonium concentrations (13 µM) corresponded to the lowest nitrate and nitrite values, as observed in the Ria of Ortigueira. As phosphate concentration decreased in flooding water (up to 0.39 µM),pore water concentrations

increased shortly (up to 2.0) after the beginning of inundation (5 minutes). Silicate in flooding water decreased gradually with the arrival of the seawater, reaching its lowest concentration (38 μM) after 20 minutes of inundation.

4. Discussion

4.1 Freshwater nutrient fluxes

On the basis of river flow and nutrient concentrations in freshwater end members of both rias, nutrient loads were estimated in two seasonal periods (Table 2). River inputs of nutrients were generally low compared with other Galician (Prego et al., 1999) and Cantabrian rivers (Prego and Vergara, 1998). These low inputs are related to the low flow of the studied rivers, which values during the sampling periods were always lower than those reported in rivers of the Western Galician Rias (Augas de Galicia, 2011). The general trend of nutrient fluxes was $H_4SiO_4 > NO_3^- > NH_4^+ > HPO_4^{2-} > NO_2^-$ for the Lourido Stream (Ria of Ortigueira) and $H_4SiO_4 > NO_3^- > NH_4^+ > NO_2^- > HPO_4^{2-}$ for the Landro River (Ria of Viveiro).

In the Lourido Stream, nutrient discharges showed no significant differences between the periods for almost all nutrients, with exception of ammonia, which increased seven times (up to 4.16 $nmol \cdot cm^{-2} \cdot d^{-1}$) in summer. Since river flow was similar in both sampling periods the flux enhancement is attributed to ammonium inputs, which may be associated with remineralization processes due to the organic nitrogen synthesized in summer (Kiefer and Atkinson, 1984; Dafner et al., 2007). In the case of the Landro River, nitrite, ammonium and silicate discharges increased more pronouncedly in May-June (up to 124 $nmol \cdot cm^{-2} \cdot d^1$ for NH_4^+). Under exceptional conditions of high river flow, nutrient fluxes may be underestimated. Fluxes may reach values up to 12 times higher than estimated for normal conditions of river flow, but these exceptional conditions represent only 2% over a year.

4.2 Nutrient fluxes between sediment and overlying water at submerged period

During the submerged period, the transport induced by diffusion of nutrients across the interface was estimated using concentration gradients between pore water of topmost sediment layer (0-2 cm) and overlying water. In general, higher diffusive fluxes of nutrient were found in the Ria of Viveiro (Table 3) were the low

porosity of the sediment may have favored the diffusive processes. This is in agreement with the findings of Manheim (1970) that showed the variation of the diffusion constant with the porosity in unconsolidated sediments. However, ammonium diffusive fluxes in the Ria of Ortigueira were higher than those estimated in the Ria of Viveiro, presumably due to the sorption of NH_4 to fine sediments. In sediments with higher organic matter content like in the Ria of Ortigueira (up to 6%), ammonium accumulation may be linked to the breakdown of fresh organic matter. Mackin and Aller (1984) showed that absorbed ammonium in marine sediments may be higher in fine-grained sediments rich in silt and clay.The negative diffusive fluxes of nitrate, nitrite and silicate in the Ria of Ortigueira in April and July indicate that nutrients were transferred from the water column into sediments.

This trend was also found in July for nitrate, ammonium and silicate in the Ria of Viveiro. The oxygen solubility reduction is directly related to the increase of temperature (Jørgensen and Revsbech, 1985), and low oxygen diffusion into sediments affects the nitrification rates. Marine sediments may be a source or sink of nitrogen (Middelburg et al., 1996); nitrification and denitrification processes, which are temperature dependent (Cartaxana et al., 1999), may explain the limited availability of nitrates and nitrites in pore water, especially during the warmer periods. Nitrate and ammonium fluxes estimated in the Northern Galician Rias were comparable with those calculated by Lerat et al. (1990) in the Bay of Morlaix (France) reporting fluxes from -3.12 to 10 $nmol \cdot cm^{-2} \cdot d^{-1}$ of nitrate and from 27 to 65 $nmol \cdot cm^{-2} \cdot d^{-1}$ of ammonium during spring-summer season.

Phosphate fluxes also showed a contrasting seasonal variation in Ortigueira and Viveiro that may be attributed to sediment type and oxygen penetration depth (Sundby et al., 2003). Sandy sediments, like those from Viveiro, are generally characterized by a thinner iron oxyhydroxide buffer layer (Krom and Berner, 1981) allowing intense exchanges across the sediment-water interface. Otherwise, in the Ria of Ortigueira the thicker oxic-suboxic sediment layer in spring act as retention to the upward diffusive phosphate flux while at summer this layer is reduced due to the increase of organic matter mineralization rates (Ishikawa and Nishimura, 1989; Falcão et al., 2006). Phosphate and silicate diffusive fluxes were low compared with the fluxes of important river-dominated estuaries (Watson et al., 1993; Mortimer et

al., 1999), but similar to those found by Al-Rousan et al. (2004) in coral reef along the Jordanian coast of the Gulf of Aqaba.

4.3 Sediment water exchanges associated to tidal flooding

Based on nutrient concentrations during tidal inundation of sandy sediments the transport across the sediment-water interface was calculated. Noteworthy and unlike diffusive fluxes, pore water transport was always positive in both sampling dates for all the nutrients studied. This clearly indicates that tidal excursion causes the export of nutrients from sediment to the water column independently of the season. Similar finding were found by Falcão and Vale (1998) in a SW European coastal lagoon and Cabrita et al.,1999 in the Tagus (Portugal) meso-tidal estuary. Minor seasonal variations were found at the Ria of Viveiro for tide-induced transport of nitrate, nitrite and phosphate (Table 3), while tide-induced transport of ammonium was almost two times higher in April than in July. In the Ria of Ortigueira, advection is limited due to the cohesive nature of the sediments. However, the variation of flooding water showed an intense exchange of nutrients between the sediment surface and the overlying water. The transport/exchange of nutrients may be calculated on the same basis as the advection. This transport was higher in April than in July for nitrate (34 times), nitrite (12 times), ammonium (3 times) and silicate (4 times), while for phosphate values remained constant (28 $nmol \cdot cm^{-2} \cdot d^{-1}$). The intense exchange of ammonium during the tidal excursion may derived from desorption from sediment particles due to the turbulence (e.g waves created by winds, river currents, etc., Corbett, 2010). Gentle mixing of seawater in the surface sediment seems to change the reversible adsorption-desorption equilibrium of ammonium in the sediment (Mackin and Aller, 1984) and causes a semi-diurnal supply of ammonium to the water column (Caetano et al., 1997). Similar results were found by Simon (1989) where changes in the sorption equilibrium of ammonium were caused by sediment resuspension induce by wind in shallow areas.

During tidal inundation, the intrusion of water rich in oxygen into the surface sediment layers may influence the pore water chemistry modifying the composition of the solutes. Kerner and Wallmann (1992), by means of laboratory experiments, found that during percolation of aerobic water in suboxic sediment, in which nitrate,

manganese and iron were the main electron acceptors, microbial oxygen reduction starts to be the main catabolic process. Changes in Fe chemistry were also reported during tidal inundation, which may have consequences over phosphate availability due to the equilibrium with freshly formed Fe oxyhydroxides (Falcão and vale, 1990; Caetano et al., 1997; Falcão et al., 2006; Serpa et al., 2007).

Although favorable upwelling conditions were found in the Northern Galician Rias during April and July (Ospina-Alvarez et al., 2010), these processes did not affect the inner part of the rias (Ospina-Alvarez et al., 2010; Prego et al. 2012), and therefore it does not contribute to the sediment-water exchange in the rias of Ortigueira and Viveiro. The high concentrations of both silicate and ammonium in pore waters (Figure 4a) may result from an increased mineralization of algal material (Conley and Johnstone, 1995) rather than fluvial input that was comparable during both sampling periods. The dissolution of the skeletons of diatoms associated with the spring bloom (Fraga, 1981; Bidle and Azam, 1999) could explain the high silica availability.

4.4 Comparison of fluvial inputs against diffusive fluxes and tide-induced transport

Tide-induced transport was always greater than diffusive fluxes for all the dissolved nutrients (rias of Ortigueira and Viveiro: Wilcoxon-Mann Whitney test, $p < 0.05$) (Table 3). The greatest differences were observed for silicate at the Ria of Ortigueira, where tidal transport was four orders of magnitude larger than diffusive fluxes. The above is consistent with other studies that have shown that advection of pore water plays an important role in the water-sediment interchange of solutes, with differences greater than two orders of magnitude between pore water advection and molecular diffusion as reported Huettel et al. (2003) in sediments with permeability higher than $10^{-12} \cdot m^2$.

The sediment-water exchange at the internal part of the Ria of Ortigueira represents 94% of its nutrient budget, by considering the fluxes from the Lourido Stream, the diffusive fluxes and tide-induced transport. In contrast, in the Ria of Viveiro the river contribution was more important but this transport account for 38% of nutrient inputs. The morphology and the sandy nature of its watershed make sediments a moderate reservoir of nutrients. In the Northern Galician Rias, tide-induced transport of nutrients was higher than in other marine and coastal areas

(Table 4), suggesting that these ecosystems are influenced by tidal processes that may determine the availability of nutrients between the sediment-water boundary and their supply to internal parts of rias. According to the above findings, an interesting avenue for future research would be the study of advective fluxes in ria systems depending on the permeability of their sediments.

5. Conclusions

This work emphasizes the importance of tidal flooding in intertidal sediments of ria-coastal systems and point out striking changes of nutrient in pore water, during short periods of inundation. These variations induce an intense transport from sediment to the water column that superimposes the nutrient contribution associated with fresh water end members. Therefore, this type of transport should be taken into account when assessing nutrient budgets in macro and meso-tidal ecosystems.

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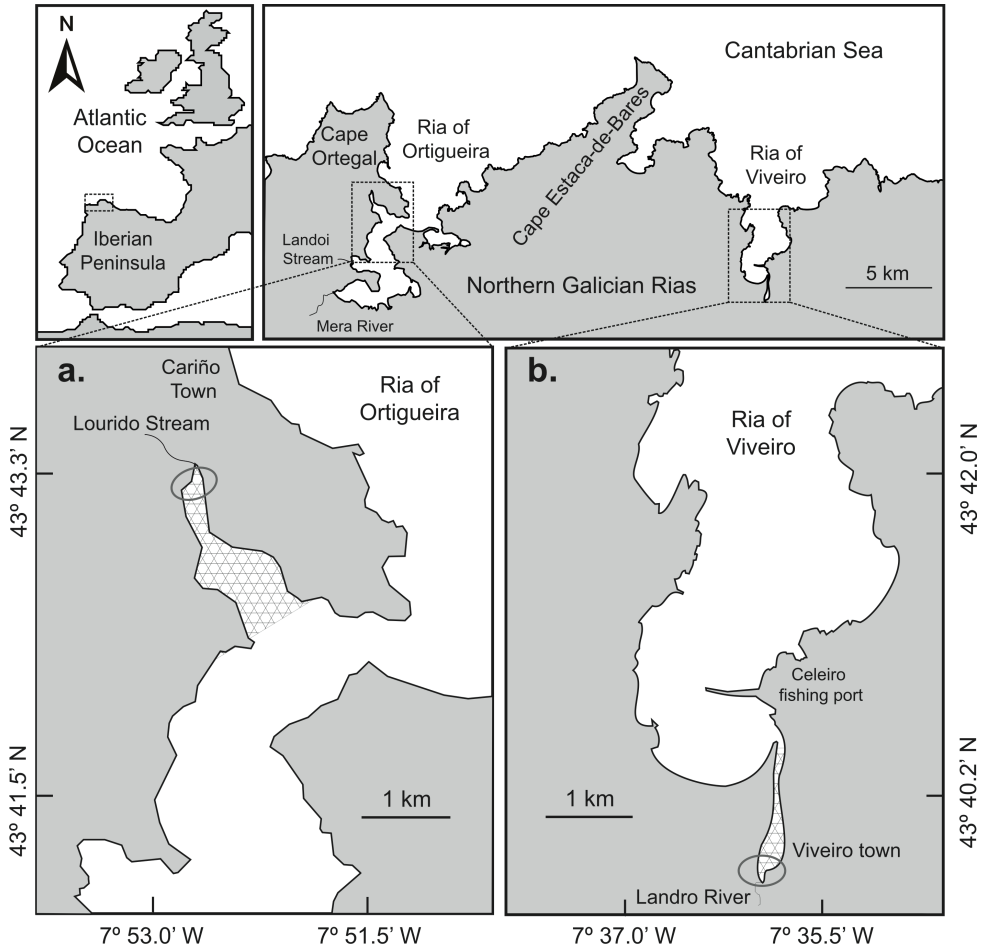


Figure 1. Map of the Northern Galician Rias, showing study area. The circular areas show the sampling stations. The areas taken into account in the calculation of fluxes are represented by a mesh gray (bottom frames, a and b) (bottom frames, a and b).

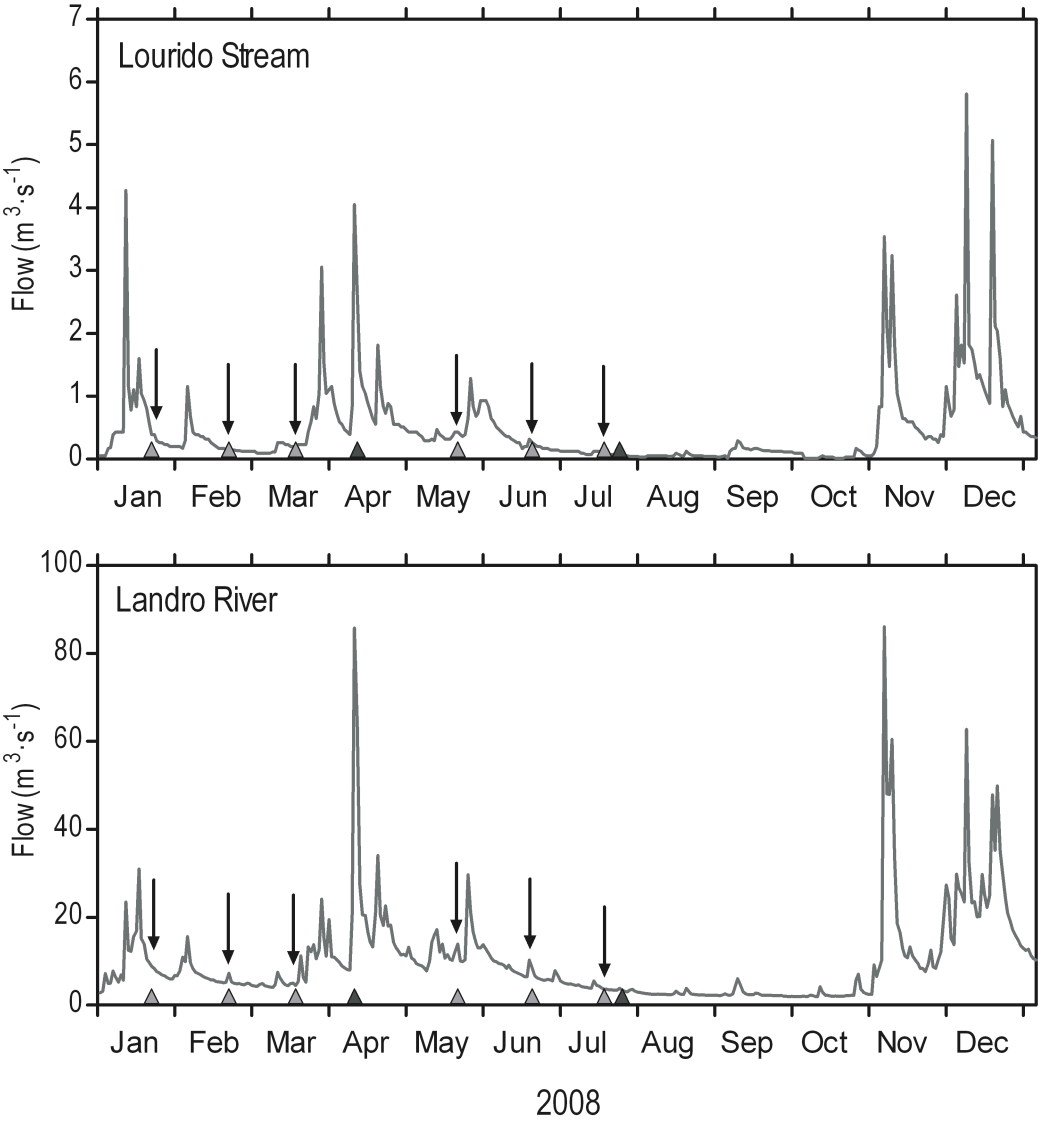


Figure 2. Daily flow ($m^{-3} \cdot s^{-1}$) of Lourido Stream and Landro River during 2008. Gray triangles correspond to the sampling dates of rivers and black triangles to the sampling dates of sediments and flooding water. Daily river flows provided by Augas de Galicia (Consellería de Medio Ambiente-Xunta de Galicia).

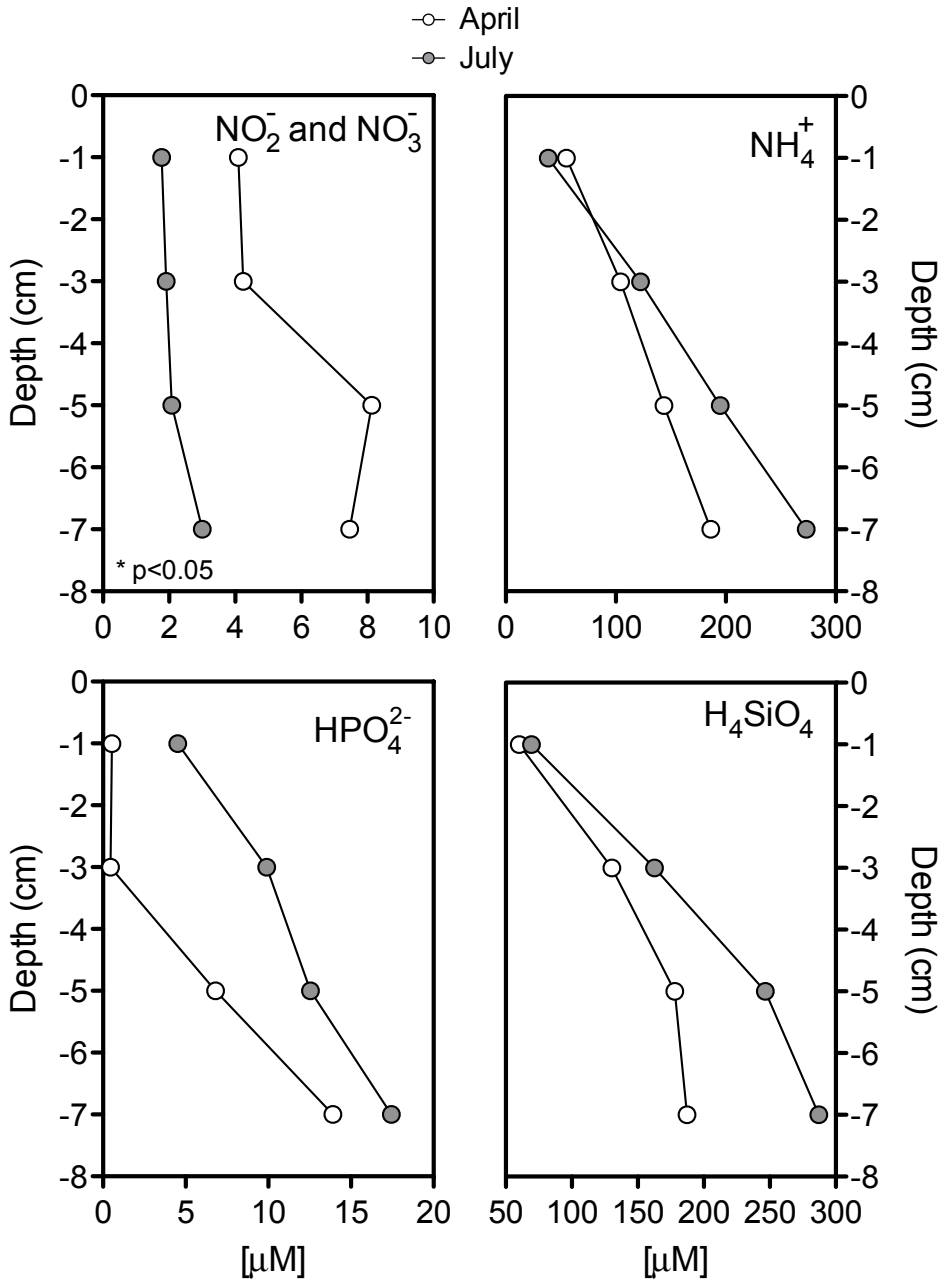
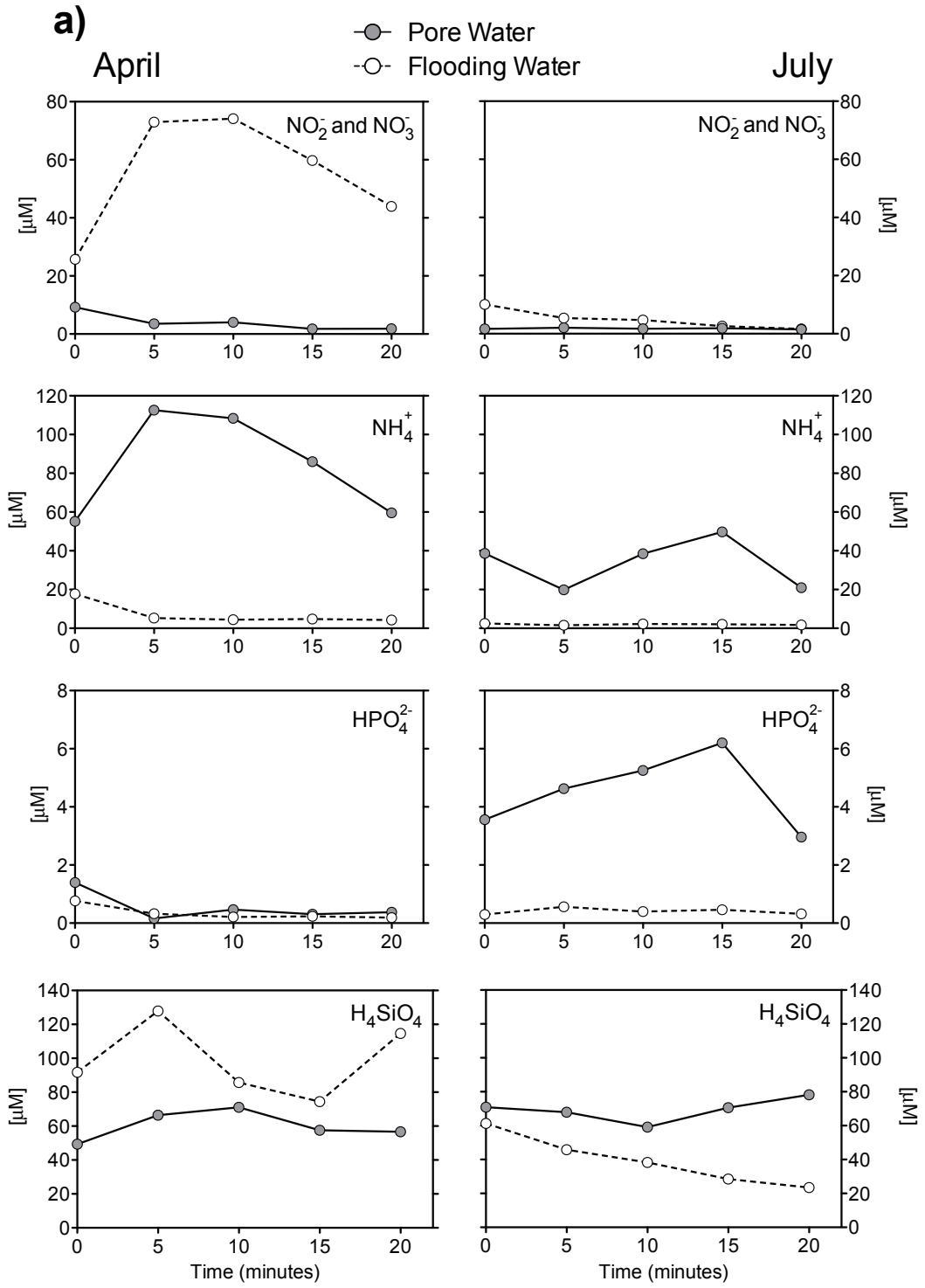


Figure 3. Vertical profiles of nutrient concentrations (μM) in sediment pore waters at air-exposed conditions at the Ria of Ortigueira during April and July 2008. p-value at the bottom-left corner of the frame indicates significant differences between samplings (Wilcoxon-Mann Whitney test).


a)
Pore Water
Flooding Water
April
July
NO_2^- and NO_3^-
NH_4^+
HPO_4^{2-}
H_4SiO_4
[µM]
Time (minutes)

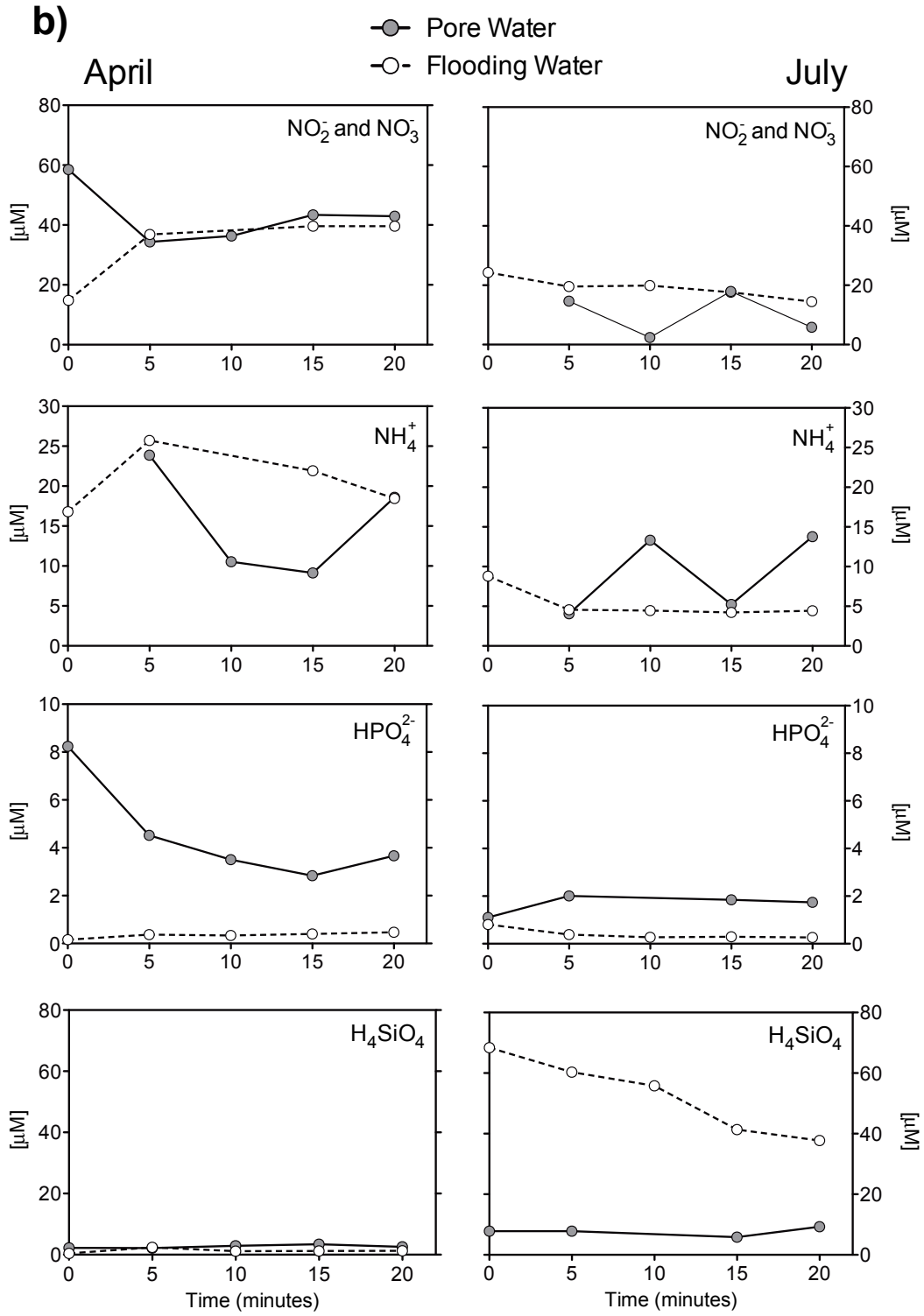


Figure 4. Nutrient concentrations (μM) in flooding and pore waters during the first 20 min of tidal inundation at the Ria of Ortigueira (a) and the Ria of Viveiro (b) in April and July 2008. Missing points correspond to samples where the volume extracted after centrifugation was not enough for analysis.

Table 1. Average nutrient concentrations of the Lourido Stream and Landro River

Nutrient	Lourido Stream		Landro River	
concentration (μM)	January-March	May-July	January-March	May-July
NO_3^-	59 (48-67)	51 (46-60)	47 (38-53)	37 (35-41)
NO_2^-	0.10 (0.06-0.15)	0.16 (0.06-0.25)	0.12 (0.07-1.16)	0.18 (0.12-0.23)
NH_4^+	0.19 (0.07-0.39)	1.46 (0.26-2.81)	0.19 (0.05-0.28)	0.63 (0.37-0.89)
HPO_4^{-2}	0.11 (<DL-0.30)	0.21 (<DL-0.43)	0.11 (<DL-0.34)	0.06 (<DL-0.11)
H_4SiO_4	263 (256-270)	269 (263-275)	141 (136-145)	165 (110-246)

Average nutrient concentrations correspond to the three months prior to the sampling of sediments and flooding water, and are given as average with the range in parentheses for the two sampling periods (January 21st to March 17th; May 19th to July 15th). DL means detection limit.

Table 2. Average nutrient fluxes from freshwater to the sampling areas of the rias of Ortigueira and Viveiro

		Lourido Stream (Ria of Ortigueira)		Landro River (Ria of Viveiro)	
	Unit	January-March	May-July	January-March	May-July
Average flow	($m^3 \cdot s^{-1}$)	0.25	0.23	6.88	8.69
*Nutrient fluxes**					
NO_3^-	($nmol \cdot cm^{-2} \cdot d^{-1}$)	186	146	7339	7448
NO_2^-	($nmol \cdot cm^{-2} \cdot d^{-1}$)	0.32	0.45	19	35
NH_4^+	($nmol \cdot cm^{-2} \cdot d^{-1}$)	0.61	4.16	30	124
HPO_4^{-2}	($nmol \cdot cm^{-2} \cdot d^{-1}$)	0.34	0.59	18	12
H_4SiO_4	($nmol \cdot cm^{-2} \cdot d^{-1}$)	825	767	22139	32811

*Fluxes are given as average values for the two sampling periods (January 21st to March 17th; May 19th to July 15t^{h}).

Table 3. Diffusive flux and tide-induced transport of nitrate, nitrite, ammonium, phosphate and silicate across the sediment-water interface of the rias of Ortigueira and Viveiro in April and July 2008

	Ria of Ortigueira		Ria of Viveiro	
	April 10th	July 21st	April 9th	July 22nd
Diffusive flux (nmol·cm^{-2}·d^{-1})				
NO_3^-	-5.15	-2.61	+11.6	-9.50
NO_2^-	-0.03	-0.06	+2.10	+0.23
NH_4^+	+30.1	+6.72	+0.73	-1.32
HPO_4^{-2}	-0.01	+0.27	+0.49	+0.15
H_4SiO_4	-2.94	-0.43	+0.22	-13.2
Tide-induced transport (nmol·cm^{-2}·d^{-1})				
NO_3^-	+5010	+146	+1500	+1450
NO_2^-	+12	+1	+5	+13
NH_4^+	+437	+140	+754	+436
HPO_4^{-2}	+28	+28	+14	+22
H_4SiO_4	+10230	+2680	+2	+4050

Positive values indicate a flux from the sediment to the overlying waters.

Table 4. Comparative table of diffusive flux and tide-induced transport of nutrients in some intertidal areas

Flux / Location	NO_3^- and NO_2^-	NH_4^+	HPO_4^{2-}	H_4SiO_4	Reference
Diffusive flux (nmol·cm^{-2}·d^{-1})					
Northern Galician Rias, Spain	-9.3 to 13.7	-1.32 to 30.1	-0.01 to 0.49	-13.2 to 0.2	This study
Ria Formosa, Portugal	nd	0.70 to 162	-0.32 to 9.20	nd	Falçao and Vale 1998 [(a)]
Bay of Morlaix, France	-4.6 to 40.1	14.8 to 72.7	nd	-0.96 to 31	Lerat et al. 1990
Gulf of Aqaba, Red Sea	0.1 to 1.1	0.1 to 3.6	0.02 to 0.40	0.5 to 1.4	Al-Rousan et al. 2004
Tamar Estuary, SW England	nd	-57.4 to 409	-18 to 55	-50 to 315	Watson et al. 1993
Humber Estuary, UK	-4450 to 1640	nd	-110 to 220	-510 to 360	Mortimer et al. 1999
Tide-induced transport (nmol·cm^{-2}·d^{-1})					
Northern Galician Rias, Spain	147 to 5030	140 to 754	14 to 28	2 to 10230	This study
Ria Formosa, Portugal	nd	7 to 142	0.20 to 31	nd	Falçao and Vale 1998 [(b)]
Island of Giglio, Italy	-71 to 531	-44 to 91	nd	66 to 175	Huettel et al. 1998 [(c)]

[(a)] Fluxes calculated from data in Fig 2 and Fig 3 in the original reference
[(b, c)] Fluxes calculated from data in Table 3 in the original reference; nd: no data.
Positive values indicate a flux from the sediment to the overlying waters.